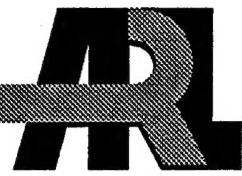


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# Volatile Organic Compound (VOC) Compliant Wash Primer

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ARL-TR-1140

July 1996

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<b>13. ABSTRACT (Maximum 200 words)</b>  DOD-P-15328 wash primer is a unique coating that passivates metal surfaces against corrosion and enhances adhesion of primers/topcoats. However, the chromate and high-solvent content subject it to strict Environmental Protection Agency (EPA) regulations. This report evaluated waterborne (WB) polymers and coating systems as in earlier investigations. Laboratory evaluations revealed a film-softening effect when topcoated with solvent-type primers due to trapped solvents in the wash primer. Wash primers formulated with VOC-exempt solvents are being tested.						
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## 1. INTRODUCTION

1.1 Background Information. The wash primer that became DOD-P-15328 was developed during World War II under U.S. Government contract by the Bakelite Company because of an urgent need for a substitute metal pretreatment in ship construction. The two-component system consisted of a zinc chromate, rust-inhibiting pigment in a flexible, adhering polymer solution activated by phosphoric acid just before use. Since its development, the wash primer has performed admirably to passivate the metal surface against corrosion and to act as a tiecoat, enhancing the adhesion of subsequent primers/topcoats. In the struggle against corrosion of tactical vehicles, the U.S. Army requires that ferrous metal surfaces be treated with a zinc phosphate immersion system or a wash primer prior to coating with an epoxy primer and a urethane camouflage topcoat.

Due to recent Environmental Protection Agency (EPA) regulations, the use of the wash primer by U.S. Army depots that refurbish older equipment has come under close scrutiny. The hexavalent zinc chromate makes the application process subject to toxic waste regulations and the high-solvent content, low-solids percent results in high volatile organic compound (VOC) content.

1.2 Objectives. Commercial vendors have unsuccessfully attempted to come up with replacements for the wash primer by formulating changes only in the pigmentation, and by going to waterborne (WB) systems with nontoxic corrosion-inhibiting pigments. So far, no one has been able to completely formulate an equivalent replacement. During FY94, an acid-tolerant WB polymer showed promising results comparable to the control wash primer. However, unacceptably long solvent retention and film softening occurred when topcoated with the solvent-type epoxy primer MIL-P-53022.

Our objective for FY95 was to evaluate WB-polymer systems that would have good adhesion to metal and good intercoat adhesion to the epoxy primer without solvent entrapment and the resultant slow cure.

## 2. EXPERIMENTAL

2.1 Reactions of the Wash Primer. The current wash primer, when activated with the phosphoric acid, performs the following three functions:

- As a dilute alcoholic solution of phosphoric acid, phosphates the metal surface.
- As a solution of chromium ions, passivates the metal surface.
- As a resin solution, seals the metal surface against corrosive attack.

The zinc chromate is basic in nature and reacts readily with phosphoric acid to form, in the presence of an organic polymer solution, a mixture of chromium in cationic and anionic forms. Chromium is available for passivating the phosphate surface with the formation of a wide scope of chelates and complexes. The most likely complex in this reaction is that of chromium with the acetal groups of the polymer in the formation of a three-dimensional organic-metallic polymer (see Figure 1).<sup>1</sup> Thus, the three processes of phosphating, passivating, and polymers sealing explain the excellent results achieved by wash primers on ferrous and nonferrous metal surfaces.<sup>2</sup>

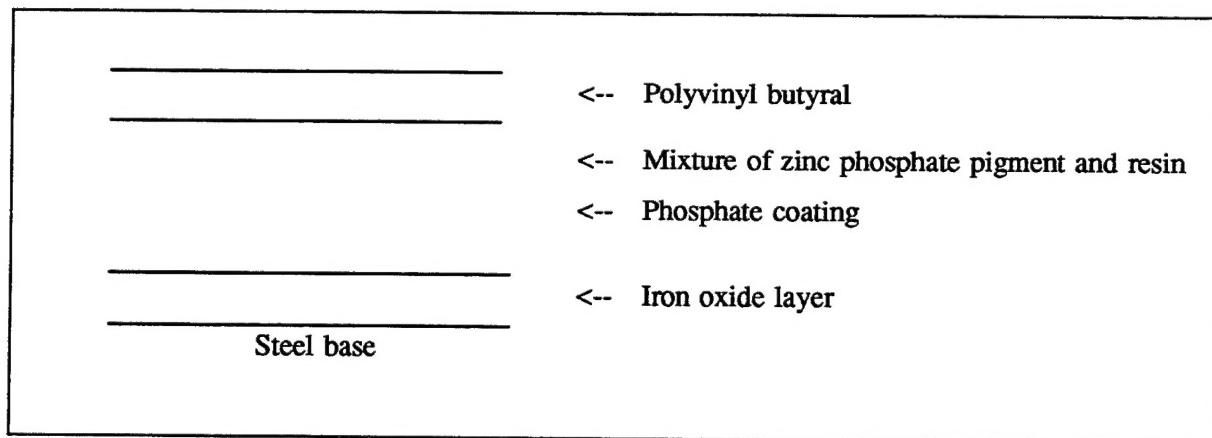


Figure 1. Stylized diagram of the wash primer film with vertical lines representing the chromium-phosphorous polymer complex.

**2.2 WB Polymers.** During the annual Paint Show and Exhibition in New Orleans in October 1994, we thoroughly canvassed all of the polymer-producing companies. This resulted in the submission of six WB, acid-tolerant polymers from four companies.

<sup>1</sup>Kruger, J., and M. C. Bloom. Industrial and Engineering Chemistry, vol. 48, pp. 1356–60, 1956.

<sup>2</sup>Chandler, R. H. Paint Technology, vol. 20, no. 7, 1973.

### **2.3 Testing.**

**2.3.1 Polymer Evaluation.** The defining test was the coating of the six polymer films with the standard solvent-type epoxy primer, MIL-P-53022, and observing the film hardness after 24 hours of air drying.

The six WB polymers were first evaluated as clear coatings with the addition of 1%, 2%, and 3% phosphoric acid reduced to half strength with water. From previous experience, we knew that 50% reduction of 85% phosphoric acid prevented shock and gelation from occurring. All six polymers tolerated the addition of reduced phosphoric acid with some variations in haze and appearance. Drawdowns on cold-rolled steel were made at 1.5 mil and 3.0 mil wet, resulting in dry films of 0.3 and 0.6, respectively. Half of the panels were air dried for 24 hours and half were air dried for 24 hours and force dried for 3 hours at 105° C. Then all of the panels were spray coated with the epoxy primer and air dried for 24 hours before evaluation of hardness. The control film of MIL-P-53022 over DOD-P-15328 was typically hard to resist film rupture by the edge of a coin. All of the WB polymers topcoated with the epoxy primer were easily ruptured by the coin's edge. At least 7 days of air drying were required to resist this coin scratch test.

Even though all of these polymers softened when topcoated with the solvent-based epoxy primer, test panels were air dried for 2 weeks and subjected to water immersion and a cyclic ultraviolet (UV)-condensate exposure of 4 hours UV at 60° C and 4 hours of condensate at 50° C. Each panel had three different areas—wash primer only, MIL-P-53022 only, and wash primer topcoated with the epoxy primer.

Initial exposure of these six polymers to 200 hours of UV condensate eliminated four systems. The best two systems were again exposed to 200 hours of UV condensate with a larger variation in film thickness. One of these WB polymers showed very good adhesion to bare metal and good resistance to rust creepage at the scribe mark. However, as noted earlier, all of these WB polymers caused the epoxy topcoat to entrap solvents and soften the film for many days.

Panels prepared as above from the two polymer systems and air dried for 2 weeks were immersed in water for 4 hours. One system showed severe softening, the other slight softening.

2.3.2 Vendors Panel Evaluation. One of the major suppliers of acrylic polymers to the coating industry submitted four formulations for evaluation, with the aim of minimizing the "softening" effect on the epoxy primer. Parts of the supplier-coated metal panels were sprayed with the epoxy primer and allowed to air dry for 3 days. Pencil hardness tests gave these results:<sup>3</sup>

Panel A + MIL-P-53022 = Greater than 6B  
Panel B + MIL-P-53022 = Greater than 6B  
Panel C + MIL-P-53022 = Greater than 6B  
Panel D + MIL-P-53022 = 3B  
Control, MIL-P-53022 = HD

As the previous data show, only one formulation showed any resistance to the softening of the coating system. However, even this improvement resulted in severe softening. The epoxy film was applied at two different thicknesses, approximately 1 mil and 2 mil dry. There was no difference in the hardness values due to epoxy-primer film thickness.

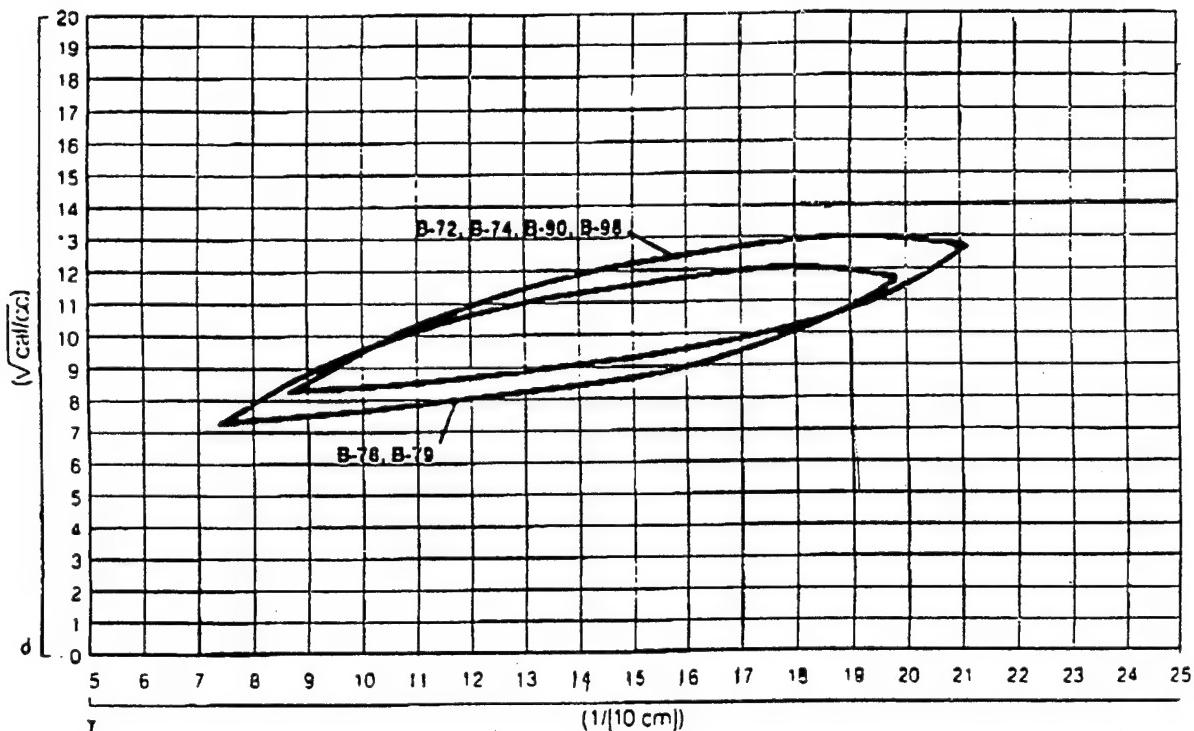
Another resistance test was run on the four panels as received. The U.S. Army uses Decontamination Solution No. 2 (DS2) to test the chemical agent resistant coating (CARC) camouflage topcoat. The coatings have to show no effect after exposure for 30 minutes in a spot test. The four panels showed these results:

Panel A = Slight softening, recovered  
Panel B = No effect  
Panel C = Severe softening, film destroyed  
Panel D = Moderate softening, recovered  
MIL-P-53022 = No effect

2.3.3 Acetone-Modified Formula. During this testing period, it was published in the Federal Register that the EPA exempted acetone as a solvent in VOC calculations. This opened up the possibility of reformulating DOD-P-15328 with the same vinyl butyral resin, but using acetone in place of isopropanol. Although the fast evaporation rate of acetone imposes limits on the formulation, various blends of acetone, butanol, water, n-methyl/pyrrolidine, and isopropanol were made and evaluated in their ability to form a clean wet and dry film using a vinyl butyral resin having the best published solubilities. Figure 2 shows

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<sup>3</sup>American Society for Testing and Materials (ASTM). "Standard Test Method for Film Hardness by Pencil Test." ASTM D3363-92a, 1992.



NOTE: In general, solvents having  $\delta$ ,  $\gamma$  within the bounded areas are solvents; those outside the area(s) are nonsolvents.

**Figure 2. Solubility of various Butvar resins plotted against solubility parameter ( $\delta$ ) and hydrogen-bonding index ( $\gamma$ ).**

the solubility parameter and hydrogen-bonding index chart for the bound areas of solubility for various vinyl butyral resins. These charts are very good predictors when various solvents have to be chosen for cost, solvency, evaporation rate, and other reasons.

From the initial laboratory formulations made with acetone, it appears possible to reformulate DOD-P-19538 at 3.5-lb/gal VOC. Once a workable formula exists at 3.5 VOC, then the chromate-pigment replacement testing can begin.

### 3. DISCUSSION AND CONCLUSIONS

Six WB polymers and the four formulated systems were evaluated for resistance to solvent absorption and entrapment when coated with the widely used U.S. Army epoxy primer. We knew at that time that another approach was necessary to solve this problem. We could not field a system that required 2 weeks

of air drying to reach a minimum hardness when the wash coat is coated with the epoxy primer. We did evaluate the water-reducible epoxy primer MIL-P-53030 by topcoating the six WB polymers. Although no problem with solvent retention and film softening was found, this combination would be only a partial solution.

The appearance of organic solvents that are not counted as VOC, such as acetone, offers the possibility to reformulate the wash primer to meet the 3.5 lb/gal VOC without changing the polymer system. This approach will be tried in FY96.

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